ACCSF 12.1 V1

To: ERT/EDISON (EPA5445)
To: ERT/GILBERT (EPA5451)
To: ERT/TURPIN (EPA5454)
To: ERT/REG.X (EPA9043)
From: ERT/PRITCHETT (EPA5462) Delivered: Wed 12-Oct-88 6:58 EDT Sys 163 (235)
Subject: TO: Jeff Webb RE: Data Validation Results For POHC Package
Mail Id: IPM-163-881012-062700396

October 11, 1988

EMAIL MEMORANDUM

SUBJECT: Preliminary Validation Results on the DRE Related Portions of the POHC Data Package

FROM: Thomas H. Pritchett, Chemist
Environmental Response Team

TO: Jeff Web, OSC
U.S. EPA Region X

I have completed my review of the quantitative portions of the POHC data package with emphasis being placed on those portions that apply to the DRE determinations. Since others are reviewing the Method 5 data and the actual DRE calculations themselves, I made no attempt to look at that portion of the whole data package. This week Tony LoSurdo of REAC will be reviewing the PIC portion of the data package.

Although I received the initial portions of the data package within approximately two weeks of the end of the test burn, that package did not contain the minimum material I needed to perform my validation or even to just confirm the "ND" determinations used in the DRE calculations. I did not receive the last essential element, the quantitation reports, until October 5. At that time, and only at that time, I was able to actually attempt to duplicate any of the quantitative determinations made in the report and I was able to confirm the absence (or less than presence) for several of the "ND" samples which contained substantial (>1 ng) peaks in the pentachlorophenol and hexachlorobenzene retention windows (which could not be defined until the supplemental data that I received on October 4) in the total ion chromatograms which were initially supplied .

Basically, several problems were noted in the package, but the data is of sufficient quality to fully support the non-detect determinations to be used in the DRE calculations for test burns 2 and 3 and of sufficient quality to support the penta-chlorophenol non-detect determination to be used in the test burn #1 DRE calculation. Although I did not fully review the actual DRE calculations, I do agree with the Method 5 reviewer that the detection limits for all components of the train should be summed prior to calculating the DRE.

My review comments are as follow:

GENERAL

1) All quantitations of actual detects are suspect based upon the data in the package. Specifically, when I manually calculated the pentachlorophenol concentrations (ng/ul in extract) for two separate samples (68290 and 68386) using the areas in the quantitation report, using the formula given in the matrix spike package, using the reported pentachlorophenol response factor of .124, and assuming a 40 ng internal standard spike, I consistently computed a concentration approximately twice the concentration reported. No deviations to the normal internal standard spike and no sample dilutions, both of which might account for these deviations, were mentioned in the extraction logs. However, when I double-checked all non-detect determinations, I did confirm these with the 40 ng internal standard spike and with the .124 pentachlorophenol response factor.

2) Although the matrix spike and matrix spike duplicate analyses met the method minimum acceptable criteria for pentachlorophenol, these analyses, with a average accuracy (or spike recovery) of 32% failed to meet the 50% accuracy QA objective targeted in Table 3-1 of the York Quality Assurance Plan for pentachlorophenol. These results cast further suspicion on any reported pentachlorophenol quantitations contained in this package. The accuracy for hexachlorobenzene and the precision for both target compounds did meet the outlined QA objectives.

TEST BURN RESULTS

3) General comments on detection limits - I reviewed the supplied documentation on the instrument detection limits. The reported 1 ng/ul detection limits were well within the capabilities of the instrument. However, because trace levels of the POHCs, and especially pentachlorophenol, were seen in many of the samples including the blanks, these detection limits can not be arbitrarily lowered unless all the data is recomputed, the new data is then retested against the lower detection limits, and finally this whole process is revalidated.

4) Test Burn #3 - All aspects of the POHC data for the byproduct samples passed for this burn.

5) Test Burn #2 - All aspects of the POHC data for the byproduct samples passed for this burn with the exception of the nitrobenzene surrogate recovery for the ash sample. This unacceptably low surrogate recovery invalidates the Non-Detect determination made for chlorobenzene in this sample. Also, as discussed in item #1, buildup of POHCs in the caustic from this test burn would be obtained from the difference between the caustic samples from test burns #2 and #3 (samples 68387 and 68283, respectively).

6) Test Burn #1 - Two separate train samples and the ash sample failed with a unacceptably low surrogate recovery. The resin and ash samples (68381 and 68385) failed to meet the minimum acceptable nitrobenzene-d5 recovery, thereby invalidating their "ND" determinations for hexachlorobenzene. The back-half sample (68380) failed to meet the minimum acceptable 2,4,6-tribromophenol recovery thereby invalidating its "ND" determination. When the results from the whole sampling train are compared against the invalidated "ND" for pentachlorophenol in the back-half sample, the "ND" results from the other two portions of the train tend to support the invalidated "ND". If pentachlorophenol had been present in the back-half at a concentration above the detection limits, one would expect that it first would have been detected in the other portions of the train as well. Unfortunately, this argument cannot be applied as strongly, if at all, to the invalidated "ND" determination for hexachlorobenzene for the XAD resin since XAD would be the portion of the trap which would be expected to trap the majority of this POHC.

FEED SAMPLES

7) The reported pentachlorophenol concentrations are at best estimates of the true concentration. First, in all cases the detected concentrations were outside the linear range of the calibration, especially when one takes into account the 2X discrepancy in the concentration calculations discussed in item #2. These results should have either been flagged as such or the samples should have been quantitatively diluted in order to bring the concentrations within the range of the calibration curve.

8) These samples contained severe levels of gross contamination as exhibited in the total ion chromatograms and as exhibited by the inability of the operator to obtain any surrogate recoveries. Without seeing the selected ion chromatograms (also known as extracted ion current profiles) I cannot determine for sure whether this contamination created a problem during the integration of the target compounds, but based upon the quantitation report I strongly suspect that it did. In addition, I would strongly question whether the relative response factors would still be valid considering that the mass spectrometer's source was being overloaded with high levels of co-eluting contamination. Regardless, because of the total absence of any surrogate recoveries, these sample extracts should have been run through an additional phenol-specific clean-up prior to being analyzed. Therefore, based upon the multiple pentachlorophenol areas reported in quantitation report, upon the absence of any surrogate recoveries, and upon the high degree co-eluting contamination, the pentachlorophenol results for the feed should be considered to be gross estimates (one significant figure) at best.

COMPLETENESS

9) Lack of the method required number of matrix spike/ matrix spike duplicate samples. Paragraph 8.6 of Method 8270, September 1986, states "the laboratory must, on an ongoing basis, analyze for each analytical batch (up to a maximum of 20 samples/batch)". York only reported one set of matrix spike/matrix spike duplicate results for an analytical batch of 31 samples. Method 8270 required that a minimum of two such of matrix spikes/matrix spike duplicates had to be run for this many samples. Under the CLP program such an omission of required QA/QC data would automatically flag the package as "non-compliant" or not meeting the terms of the contract on major deliverables. Such packages must then be reviewed by the agency within a designated time period (30 days?) in order to determine whether or not the agency is even willing to accept any of the data package for use and for invoicing.

10) Duplicate train results? Tables 3-1 and 4-2 of the York QA project plan clearly imply that there should have been a set of duplicate results reported although these samples were not readily apparent in the chain of custody. However, since I was initially focusing just on the dioxin/furan portion of sampling during the on-site meetings, this requirement could have been dropped with the EPA's consent and I did not have that decision in my notes. The transcripts and notes for these meetings should be checked for such a agreement because the absence of such data causes York to fail their 90% data complete criteria and well as once again making the data non-compliant.

CONCLUSIONS

The final, quantitative POHC data package contained several severe problems, at least one of which constituted grounds for automatic rejection. All the quantitations are suspect for either computation errors, being outside the calibration range, or containing such high degree of matrix interference that even the instrument response is questionable (yet alone the actual integration accuracy). However even with all of these problems the data is usable to compute DRE values from the test burn since only the non-detect determinations have a significant effect on the final DRE; the amount of native pentachlorophenol was insignificant compared the amounts being spiked into the feed.

cc: R. Turpin
J. Gilbert

Jeff:

An additional note which I did not want to include in this document but which may be of significance in the upcoming cost negotiations between the EPA, Riedel, and Vesta.

You might want to explore further the issue of a non-compliant data package. There are established obligations and time windows

for the EPA and a laboratory when a non-compliant data package is submitted to the EPA for validation under the CLP. If I remember correctly the EPA has ten days to initially review the data to determine if a package is complete (or compliant). The laboratory then has a fixed time period (two weeks?) in which they can correct the package. At the end of that period the EPA has an additional thirty days to determine whether the data package is of acceptable quality for use before we lose our option of totally rejecting the package, sending all the data back, and cancelling all payment. Several of these stages and time windows have been challenged and upheld in court. Although we were never intending to reject the data package except as a last resort, you should be able to argue that Vesta's submittal of a non-compliant, grossly incomplete data package caused these time windows to operable for us. If such time deadlines did become operative, then we, the EPA, have met, and are continuing to meet, our obligations to Vesta to make our appropriate decisions in a reasonable timely manner.

Dottie:

File this memo as is under American Crossarms, Chehalas WA.
Thanks, Tom

Disposition: